Relativistic calculations of $K\alpha$ satellite properties for medium-Z elements

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(Received 20 August 1990; revised manuscript received 3 May 1991)

Relativistic Dirac-Fock calculations of the $K\alpha$ satellite lines for several elements having atomic numbers between 19 and 32 are presented along with the results from nonrelativistic Hartree-Fock calculations. Relative intensities and energies are compared with experimental results and a previous calculation. Generally good agreement is found with some deviations.

I. INTRODUCTION

Satellite lines in the $K\alpha$ x-ray spectra have been observed for many years and a general understanding of their origin has been known for nearly as long. Wentzel [1] and Druyvesteyn [2] proposed that the satellites were the result of transitions in the presence of spectator holes in the L shell: $(1s2s)^{-1}\rightarrow(2p2s)^{-1}$ and $(1s2p)^{-1}\rightarrow(2p)^{-2}$. Early calculations [3] were not accurate enough to provide accurate transition assignments to the observed satellites, although many attempts were made. Recently, Kuhn and Scott [4] (KS) reexamined the problem for all the elements for which Parratt [5] presented results in his pioneering paper. KS attacked this problem with powerful modern computers and the excellent nonrelativistic Hartree-Fock program of Froese Fischer [6]. Their results illuminated the difficulties that earlier attempts to fit satellite lines, using only energy calculations and single elements, had encountered. In order to make satisfactory transition assignments it was necessary to calculate line intensities and to compare results for several elements so as to ascertain trends.

Although the results of KS fit Parratt's data well for all elements from K ($Z=19$) through Ge ($Z=32$), theirs was not a first-principles calculation. Because nonrelativistic approximations were made, it was not possible to calculate absolute energies with sufficient accuracy—empirical $K\alpha_1$ and $K\alpha_2$ energies had to be used. See Ref. [4] for details. Since that time, Maskil and Deutsch [7] (MD) have presented new data and relativistic calculations for Cu. Although their experimental data are very close to Parratt's, their calculated results differ considerably from those of KS. For that reason, it seems appropriate to reconsider the results of Parratt and KS using completely relativistic calculations.

II. CALCULATIONS

All of the relativistic calculations reported in this work were made using the Dirac-Fock computer program of McKenzie, Grant, and Norrington [8], slightly modified to run on a Cyber 960. All calculations were run in the extended average-level optimization scheme and included first-order transverse Breit, second-order vacuum polarization, and approximate self-energy contributions. In order to obtain results with near-eV accuracy, all of these corrections are necessary. Although the program allowed one to choose a uniform charge distribution for the nucleus, we used a point nucleus because (a) the difference between point nucleus and uniformly charged nucleus calculations was of the order of 0.1 eV for all of the elements considered, and (b) the point nucleus gave better results for $K\alpha_1$ and $K\alpha_2$ energies.

In order to check the program and to assess the level of accuracy to be expected, we calculated the $K\alpha_1$ and $K\alpha_2$ energies for many of the elements with atomic number between 19 and 32. The calculated results agreed with the experimental results tabulated by Bearden [9] to within 1 eV for all elements except Ca, where the deviation was 2 eV. We conclude that our calculations should be accurate to 1–2 eV.

The line intensities are most naturally calculated in j-j coupling when relativistic calculations are being made. We consider only configurations which have all closed shells except for the $1s$ and $2p$ shells. The angular-momentum coupling of the basis states is shown in Table I for the initial and final states of the $(1s2p)^{-1}\rightarrow(2p)^{-2}$ transition. We have suppressed reference to the closed shells. (We neglect the $2s$ spectator hole transitions because of their small contribution to the satellite spectrum [4].) The intensity, summed over initial and final states and polarizations, is proportional to the square of the re-

TABLE I. Definition of the basis states. $\bar{p}$ is used to indicate the $p_{1/2}$ orbital, while p designates the $p_{3/2}$ orbital.

Initial state $(1s,2p)^{-1}$
$\lvert i_1\rangle=\lvert\{[s_{1,2},(\bar{p})^2_0]_{1/2},(p^3)_{3/2}\}_2\rangle$
$\lvert i_2\rangle=\lvert\{[s_{1,2},(\bar{p})^2_0]_{1/2},(p^3)_{3/2}\}_1\rangle$
$\lvert i_3\rangle=\lvert\{[s_{1,2},(\bar{p})_{1/2}]_0,(p^4)_0\}_0\rangle$
$\lvert i_4\rangle=\lvert\{[s_{1,2},(\bar{p})_{1/2}]_1,(p^4)_0\}_1\rangle$
Final state $(2p)^{-2}$
$\lvert f_1\rangle=\lvert\{[(s_{1/2})^2_0,(\bar{p})^2_0]_0,(p^2)_2\}_2\rangle$
$\lvert f_2\rangle=\lvert\{[(s_{1/2})^2_0,(\bar{p})^2_0]_0,(p^2)_0\}_0\rangle$
$\lvert f_3\rangle=\lvert\{[(s_{1/2})^2_0,(\bar{p})_{1/2}]_{1/2},(p^3)_{3/2}\}_1\rangle$
$\lvert f_4\rangle=\lvert\{[(s_{1/2})^2_0,(\bar{p})_{1/2}]_{1/2},(p^3)_{3/2}\}_2\rangle$
$\lvert f_5\rangle=\lvert[(s_{1/2})^2_0,(p^4)_0]_0\rangle$

duced matrix element (we consider dipole radiation only and neglect the contributions to the relative intensities from the small energy differences of the transitions in the complex),

$$I_{i\to f}\sim|(f\|O^{(1)}\|i)|^2 . \tag{1}$$

Using the results of Grant [10] and techniques developed by Racah, we have calculated the reduced matrix elements for the irreducible rank-one tensor operator of Eq. (1) for the basis states of Table I. The results are presented in Table II, where we have used an abbreviated notation for the single-particle reduced-matrix elements:

$$\langle p_{3/2}\rangle\equiv(1s_{1/2}\|O^{(1)}\|2p_{3/2}) = -\sqrt{4/3}M_{\rm ab}(p_{3/2}) , \tag{2}$$

$$\langle p_{1/2}\rangle\equiv(1s_{1/2}\|O^{(1)}\|2p_{1/2}) = -\sqrt{2/3}M_{\rm ab}(p_{1/2}) . \tag{3}$$

The square of these matrix elements would give the relative intensity of the corresponding transitions if the actual states were the pure j-j coupled states. The relativistic Dirac-Fock program (RDF) gives the expansion coefficients of the atomic states in terms of the chosen basis. From these expansion coefficients, one may determine the computed relative line intensities

$$|i\rangle=\sum_r C_r^i|i_r\rangle , \tag{4}$$

$$|f\rangle=\sum_s C_s^f|f_s\rangle , \tag{5}$$

$$I_{i\to f}\sim\left|\sum_{r,s}C_s^fC_r^i(f_s\|O^{(1)}\|i_r)\right|^2 . \tag{6}$$

The matrix elements $M_{\rm ab}(p_{3/2})$ and $M_{\rm ab}(p_{1/2})$ are defined by Grant [10] in terms of integrals involving the spherical Bessel functions and the radial wave functions of the s and p orbitals and the gauge in which one is working. The gauge is specified by a parameter G. Two gauges are particularly interesting: the Coulomb gauge ($G=0$), which corresponds to the velocity form of the radiation matrix element in the nonrelativistic limit, and the Babushkin gauge ($G=\sqrt{2}$ for dipole transitions), which gives the length form. Although the intensities cannot depend on the gauge if exact wave functions are used, there may be differences in practical work. For this reason, we have considered both of the above gauges which look much different in practice. Matrix elements in the length-form gauge are denoted simply $M_{\rm ab}$, while those in the velocity-form gauge are denoted $MV_{\rm ab}$. From Grant's work one can show that

$$M_{\rm ab}(p_{3/2})=i3\sqrt{2}(J^1+I_2^-+I_2^+/2) , \tag{7}$$

$$M_{\rm ab}(p_{1/2})=i3\sqrt{2}(J^1+I_2^--I_2^+) , \tag{8}$$

$$MV_{\rm ab}(p_{3/2})=i\sqrt{2}(I_0^-+I_2^--I_0^++I_2^+/2) , \tag{9}$$

$$MV_{\rm ab}(p_{1/2})=i\sqrt{2}(I_0^-+I_2^-+2I_0^+-I_2^+) . \tag{10}$$

The integrals J^1 and $I_L^\pm$ are defined by Grant [10]. In order to test the effect of the choice of gauge as well as investigate the difference between the $p_{3/2}$ and $p_{1/2}$ contributions to the intensity calculations, we have evaluated the integrals of Eqs. (7)–(10) using the code of McKenzie *et al.* [8]. The calculations were performed for Cu assuming that the $4s$ electron would be absent, as is appropriate for this metal. The $1s$ and $2p$ orbitals were calculated from separate runs using the appropriate configurations in each case. The results are presented in Table III, where we have divided out the common factor, $\sqrt{2}i$. From the table one can see that gauge invariance is preserved to better than 0.5%, while the difference between the $p_{3/2}$ and $p_{1/2}$ integrals is only about 1.5%.

The near equality of the $p_{3/2}$ and $p_{1/2}$ integrals enables us to make a great simplification. If one assumes equality, the integrals cancel when computing relative intensities and do not have to be evaluated—only the expansion coefficients of Eqs. (4) and (5) are required. By substituting Eqs. (2) and (3) into Table II, assuming equality of the

TABLE II. The reduced matrix elements for an irreducible tensor operator of order 1 in the basis set of Table I.

	$\|i_1\rangle$	$\|i_2\rangle$	$\|i_3\rangle$	$\|i_4\rangle$
$\langle f_1\|$	$\sqrt{5/4}\langle p_{3/2}\rangle$	$-\sqrt{5/4}\langle p_{3/2}\rangle$	0	0
$\langle f_2\|$	0	$\sqrt{1/2}\langle p_{3/2}\rangle$	0	0
$\langle f_3\|$	$-\sqrt{5/4}\langle p_{1/2}\rangle$	$-\frac{1}{2}\langle p_{1/2}\rangle$	$-\sqrt{1/2}\langle p_{3/2}\rangle$	$\frac{1}{2}\langle p_{3/2}\rangle$
$\langle f_4\|$	$\sqrt{5/4}\langle p_{1/2}\rangle$	$\sqrt{5/4}\langle p_{1/2}\rangle$	0	$\sqrt{5/4}\langle p_{3/2}\rangle$
$\langle f_5\|$	0	0	0	$\langle p_{1/2}\rangle$

TABLE III. Radial integrals calculated for Cu with a vacant $4s$ orbital. All quantities are in atomic units ($\hbar=e=m_e=1$).

	$p_{1/2}$	$p_{3/2}$
J^1	0.029 734	0.029 613
I_0^+	−0.000 477	−0.065 300
I_0^-	0.090 361	0.023 284
I_2^+	−0.000 096	−0.000 233
I_2^-	0.000 226	0.000 085
$M_{\rm ab}/\sqrt{2i}$	0.090 166	0.088 744
$MV_{\rm ab}/\sqrt{2i}$	0.089 729	0.088 552

TABLE IV. The line-strength matrix elements for the $(1s2p)^{-2}\to(2p)^{-2}$ transition under the assumption that $M_{\rm ab}(p_{3/2})=M_{\rm ab}(p_{1/2})$. All common factors have been removed since we are interested only in relative intensities. The square of an element gives the intensity for pure j-j coupling.

	$\|i_1\rangle$	$\|i_2\rangle$	$\|i_3\rangle$	$\|i_4\rangle$
$\langle f_1\|$	$-\sqrt{5/3}$	$\sqrt{5/3}$	0	0
$\langle f_2\|$	0	$-\sqrt{2/3}$	0	0
$\langle f_3\|$	$\sqrt{5/6}$	$\sqrt{1/6}$	$\sqrt{2/3}$	$-\sqrt{1/3}$
$\langle f_4\|$	$-\sqrt{5/6}$	$-\sqrt{5/6}$	0	$-\sqrt{5/3}$
$\langle f_5\|$	0	0	0	$-\sqrt{2/3}$

$p_{3/2}$ and $p_{1/2}$ matrix elements, and eliminating common factors which cancel in computing relative intensities, we obtain the results of Table IV. This table can be used, along with the calculated mixing coefficients, to calculate easily the relative intensities with good accuracy.

III. RESULTS

Because the calculations of KS fit the experimental data so well over the range $Z=19$–32, it was surprising to us that the relativistic calculations for Cu of Maskil and Deutsch [7] disagreed. We have repeated their calculation using the same program [8] in order to ascertain the root of the discrepancy. Our energies are consistently about 3 eV higher than theirs and our relative intensities differ greatly for some lines. We believe that these different results may lie in differences in the way the code was used by MD and by us. We calculated energy levels for each configuration separately, first calculating the initial levels, then the final levels on a separate computer run and subtracting the results to obtain the line energies. We believe that MD input data for both initial and final states into the *same* computer run and used the results of this calculation to compute the line energies. Since both groups used the extended average-level optimization scheme, these different modes of input produced slightly different energy levels. When computing the $K\alpha_1$ and $K\alpha_2$ energies, our technique gave values within 0.2 eV of the experimental values of Bearden, while the procedure we believe that MD used gave line energies about 3.4 eV too large. This 3.4 eV was then subtracted from MD's calculated satellite line energies to give the values presented in their paper—values about 3 eV smaller than those we calculate using the same code, but a different input procedure. (Coincidentally, although the two inputting procedures give results differing by about 2 eV for the initial and final energy levels of the states involved in the satellite transitions, the differences cancel when computing the line energies so that both procedures would have given almost identical line energies had MD not made the 3-eV correction.)

The 3-eV calculational difference in the two procedures is intolerable in a calculation needing 1- or 2-eV accuracy. We believe that the individual energy-level values obtained by asking the code to optimize over a group of levels separated by only 20 or so eV are surely more accurate than if that optimization is taken over levels spaced 8000 eV apart. That is, we believe our calculations for the line energies to be more accurate than those presented by MD, their values being about 3.4 eV too low.

Our intensity calculations also differ from theirs, but, since they presented no information on their method of calculation, we cannot speculate on the reason for the difference. We just note here that our results show reasonable agreement with the nonrelativistic calculations and with the experimental data on Cu and the several other elements studied.

These differences are clearly seen in Table V, where we present our new relativistic calculations along with those of MD and the nonrelativistic results of KS. The notation used to designate the lines is from KS. In addition, we have specified the transitions involved by naming each level according to the dominant component (in Cu) of the basis set of Table I. Thus the energy level labeled $|1\rangle$ has as its dominant component the basis state $|i_1\rangle$. The final states are similarly noted, except that their index has been increased by 4, i.e., the dominant component of state $|6\rangle$ is $|f_2\rangle$. This notation generally puts the initial and final states in order of increasing energy (see Fig. 1).

In Fig. 2, we display the calculated results of MD along with our new calculations and the results of Parratt. [We have not displayed the transition designated α'' by Parratt because it is a $(1s3p)^{-1}\rightarrow(2p3p)^{-1}$ transition.] It is seen that our results are in better agreement

TABLE V. Relativistic and nonrelativistic calculations of the energies and relative intensities of the $K\alpha$ satellite lines for Cu with no 4s electron. The KS results are from Ref. [4] while the MD results are from Ref. [7]. All energies are in eV.

		Energies			Intensities		
		This work	MD	KS	This work	MD	KS
a	$\|4\rangle\rightarrow\|8\rangle$	8083.9	8080.7	8084.5	1.00	1.00	1.00
b	$\|1\rangle\rightarrow\|5\rangle$	8078.8	8075.9	8078.2	0.80	0.49	0.81
c	$\|2\rangle\rightarrow\|5\rangle$	8088.7	8085.6	8087.5	0.43	0.42	0.43
d	$\|1\rangle\rightarrow\|7\rangle$	8060.9	8058.0	8060.6	0.31	0.19	0.31
e	$\|4\rangle\rightarrow\|9\rangle$	8054.7	8051.5	8055.9	0.25	0.25	0.25
f	$\|3\rangle\rightarrow\|7\rangle$	8085.9	8083.0	8084.0	0.25	0.75	0.25
g	$\|2\rangle\rightarrow\|6\rangle$	8075.5	8072.3	8074.6	0.25	0.25	0.25
h	$\|2\rangle\rightarrow\|7\rangle$	8070.8	8067.7	8069.9	0.14	0.14	0.14
i	$\|1\rangle\rightarrow\|8\rangle$	8050.3	8047.4	8049.8	0.13	0.08	0.13
j	$\|2\rangle\rightarrow\|8\rangle$	8060.2	8057.1	8059.0	0.11	0.13	0.12
k	$\|4\rangle\rightarrow\|7\rangle$	8094.5	8091.3	8095.4	0.05	0.05	0.05
l	$\|4\rangle\rightarrow\|5\rangle$	8112.4	8109.2	8112.9	0.01	0.01	0.01
m	$\|4\rangle\rightarrow\|6\rangle$	8099.2	8095.9	8100.1	0.00	0.00	0.00
n	$\|2\rangle\rightarrow\|9\rangle$	8031.0		8030.4	0.00		0.00

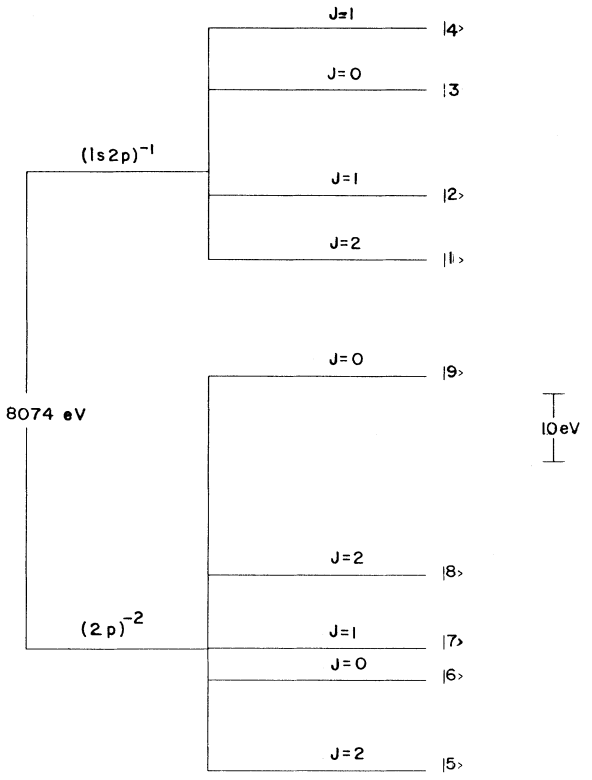


FIG. 1. The energy levels involved with the $K\alpha$ satellite transitions calculated for Cu with a missing $4s$ electron using the RDF program of Ref. [8]. The calculation included first-order transverse Breit corrections as well as second-order vacuum polarization and approximate self-energy contributions.

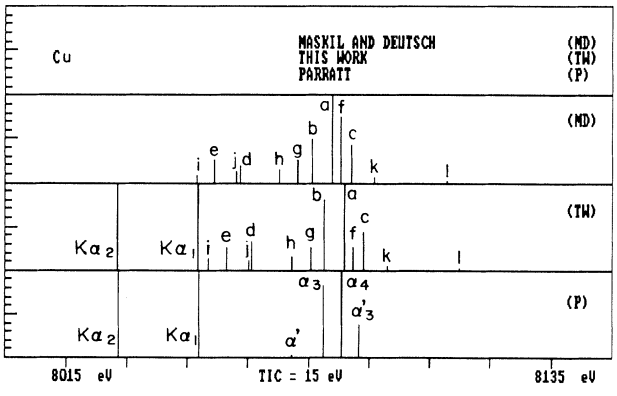


FIG. 2. $K\alpha$ satellite relative intensities as a function of transition energy in eV. For comparison, the $K\alpha_1$ and $K\alpha_2$ energies (Ref. [9]) are presented as well (intensities not to scale)—they are the two long lines at the left. The bottom set of lines shows Parratt's experimental data (Ref. [5]), the middle set gives our RDF calculated results, while the top set of lines gives the results of MD (Ref. [7]). As shown on the abscissa, the tic marks are 15 eV apart.

with those of Parratt than are those of MD. (Note that we have argued above that the energy calculations presented by MD should be shifted upward in energy by about 3 eV, improving their agreement with Parratt's data.) MD also presented new experimental data on the Cu satellite lines as well as a four-line decomposition which enables us to connect their data with those of Parratt. Since their decomposition-line energies differed from those determined by Parratt by about 1.2, 1.0, 0.7, and 0.9 eV, with Parratt's values always larger, and our calculations are only accurate to 1 or 2 eV, we have not presented them here; however, shifting Parratt's data to the left by 1 eV in Fig. 2 and interchanging the intensities of α_3 and α_4 will enable one to facilitate comparison with their new data as well. MD postulated new transition assignments on the basis of their calculations. Their assignments must be reconsidered on the basis of their calculations reported here, which agree with the previous results of KS.

Because these energy calculations are not expected to provide transition energies with an accuracy better than 1–2 eV, it is risky to base specific assignments on the results for a single element. KS developed their assignments by considering all of the elements with atomic numbers between 19 and 32. With this in mind, we have recalculated the $(1s2p)^{-1} \rightarrow (2p)^{-2}$ complex for Ca, Ti, Fe, Ni, Cu, and Zn—all those elements within this range for which closed-shell configurations can reasonably be assumed (except for the active shells, of course). Our purpose is to investigate the validity of the nonrelativistic approach and to ascertain whether new transition assignments need to be made. The results are displayed in Fig. 3, where we show the nonrelativistic results of KS, Parratt's experimental results, and the calculated RDF results from this work.

It may be seen that, although the agreement with the nonrelativistic calculations is generally good, there are instances of different ordering of some lines. For example, in K and Ca, the relativistic and nonrelativistic calculations yield lines g and h in different energy order. This occurs because of small differences computed for the energies of levels 6 and 7. These levels are very close together in these atoms and the relativistic calculation puts level 6 higher than level 7 for K, Ca, and Ti, whereas the nonrelativistic calculation has level 7 always higher in energy. (Note: we are talking about energy differences of the order of 1 eV here.) Similarly, differences in the energy levels of 1 or 2 eV between the relativistic and nonrelativistic calculations can result in a different energy order for some lines, e.g., a and f in Fe, Ni, Cu, and Zn. Except for Ti, where lines a and c are very close in energy, the order change occurs when one of the lines is weak, so the perceived structure of the complex is similar for both sets of calculations.

Although the results for K, Cu, Zn, Ga, and Ge are in good agreement with both the experimental results and the nonrelativistic calculations, generally being within 1 or 2 eV of the other results, those for Ca, Ti, Fe, and Ni are not so good. In each of these, the Dirac-Fock results lie about 2 eV below the Hartree-Fock results. This can be traced to the poor values obtained for the parent lines

themselves—the $K\alpha_{1,2}$ transitions. If the differences between the experimental and theoretical $K\alpha_{1,2}$ lines were added to the calculated results (as was the method used by KS to obtain their nonrelativistic results) then the relativistic and nonrelativistic calculations would be in good agreement with each other and with Parratt's data, with the exception of Ti [11,12]. Even with the aforementioned discrepancies, it is remarkable that the experimental data can be fitted so well with a first-principles calculation with *no* adjustable parameters.

IV. CONCLUSIONS

The primary motivation of this work was to understand why the relativistic calculations of the $K\alpha$ satellite lines, as reported by MD, differed so much from the nonrelativistic results of KS, and to compare relativistic results with nonrelativistic calculations. We have not been able to reproduce MD's intensity results, although we believe we understand why their energy calculations differ from ours. Our RDF results are very similar to the nonrelativistic results of KS.

MD's paper presented new high-resolution measurements of the $K\alpha$ satellite complex for Cu. From the shape of the spectrum, they identified seven features (A–G), although the multitude of free parameters involved in a least-squares fit to the data prevented them from an unambiguous resolution of those features into individual lines. Four of those features were related to the previous designation of Parratt, $A \rightarrow \alpha'$, $D \rightarrow \alpha_3$, $E \rightarrow \alpha_4$,

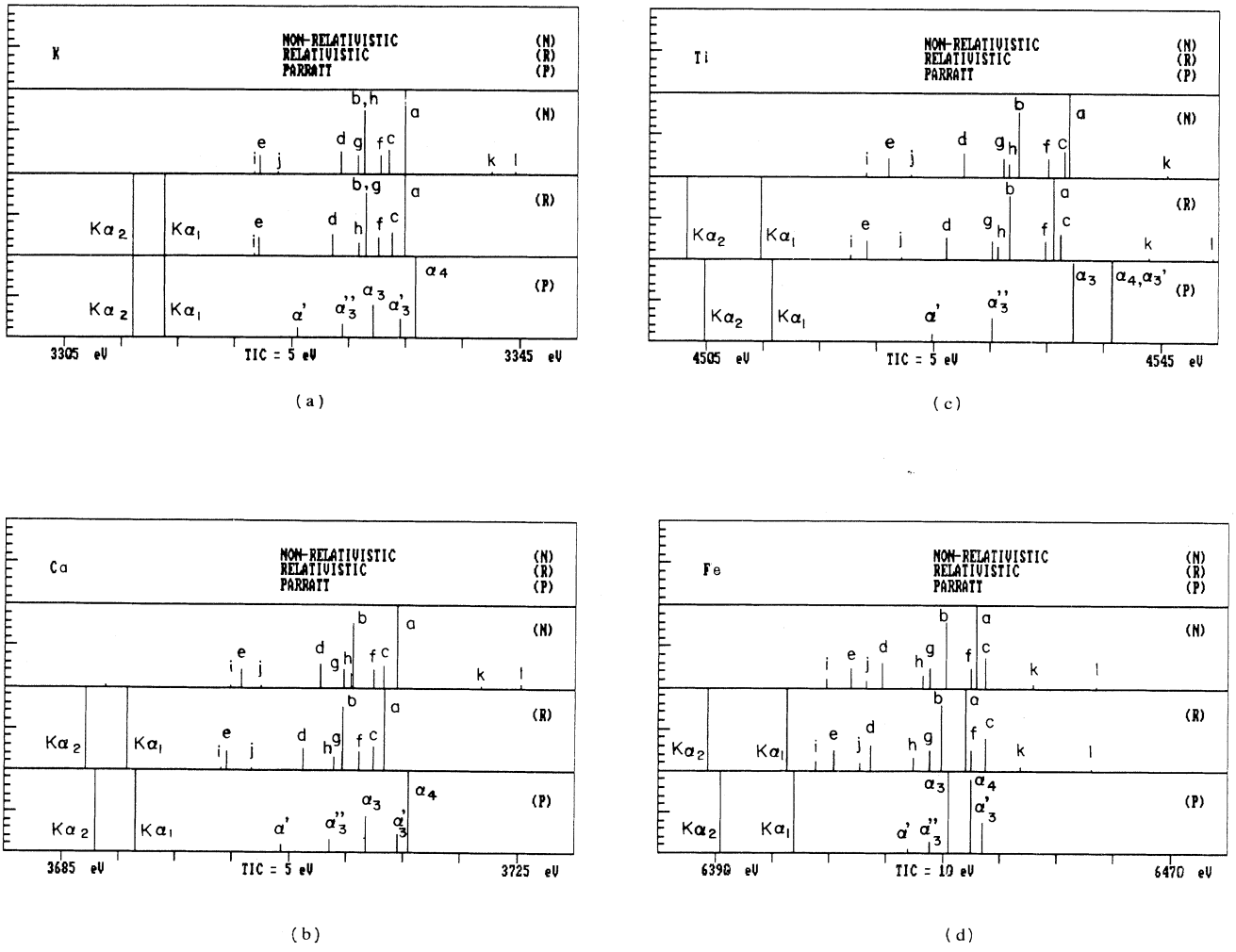
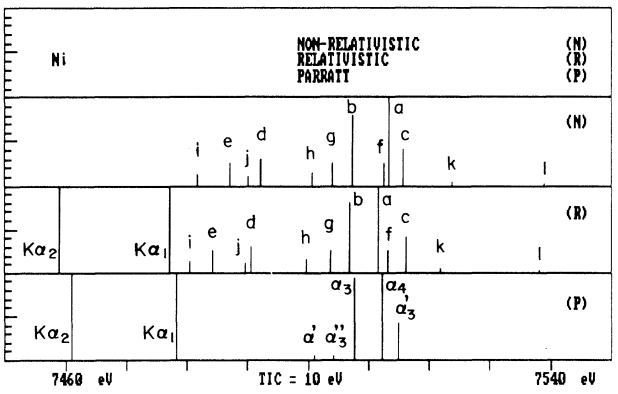


FIG. 3. $K\alpha$ relative intensities as a function of transition energy in eV. For comparison, the $K\alpha_1$ and $K\alpha_2$ energies (Ref. [9]) are presented as well (intensities not to scale)—they are always the two long lines at the left of each figure. In each figure, the bottom set of lines shows Parratt's experimental data (Ref. [5]), the middle set gives our RDF calculated results, while the top set of lines gives the results of Ref. [4]. Since the separation of the tic marks varies from graph to graph, we have noted the separation on the abscissa.

and $F \rightarrow \alpha_3'$, while the others (B, C, and G) were newly identified. As a result of their calculations, MD made transition assignments to the above structures, some of which are substantially different from those made previously. For example, MD assign the line a to D and f to E, while KS assign a and f to E and b to D, in substantial agreement with the results of this work. MD assign line b to a new feature C, which corresponds well with line g



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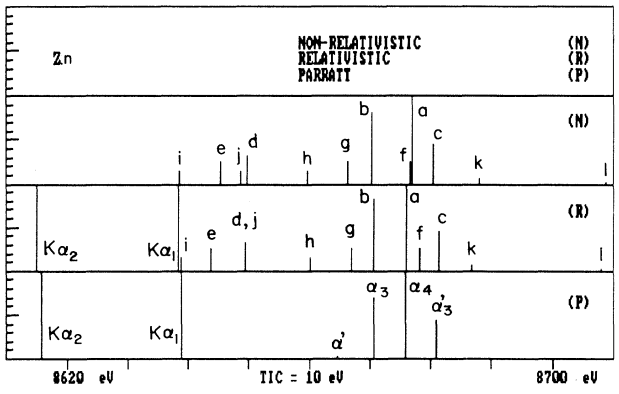

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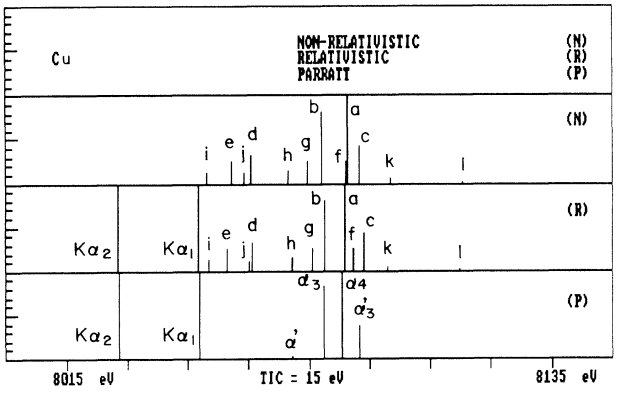

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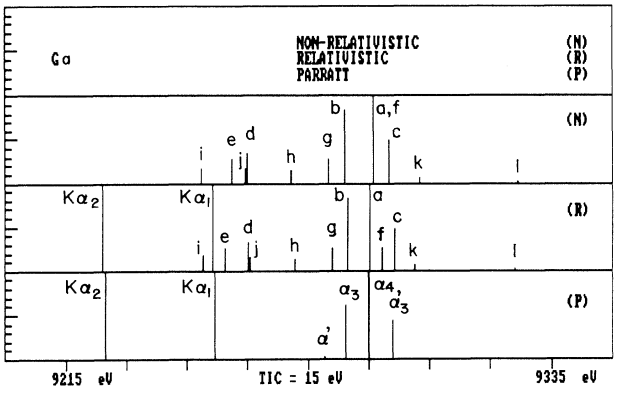
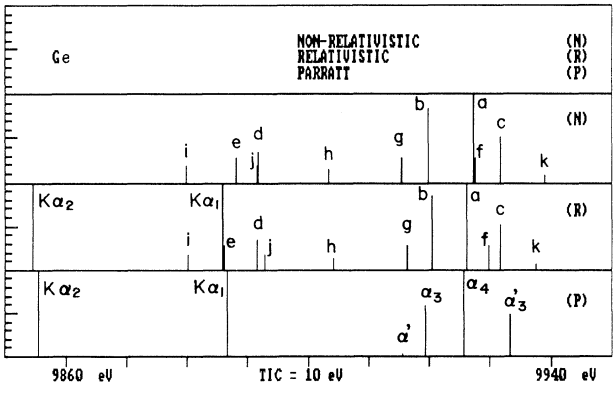


(h)



(i)

FIG. 3. (*Continued*).

of this work. We agree with their assignment of line c to F (although f may also contribute to this structure) and of h to A. Table VI contains a summary of these assignments. Note that this work suggests a line assignment for structure B which lies midway between our lines h and g. In light of the discrepancies noted above between line energies reported in this work and those used by MD, as well as the substantial differences in the two calculated sets of relative line intensities, the detailed assignment of transitions to $K\alpha$ satellite spectral features must await more exact calculations. A tenth-of-an-eV accuracy may be required to settle this question.

Although the results of this work disagree substantially with that of MD, our results support the assignments of KS, except that in Cu, Zn, Ga, and Ge transition f could more likely be assigned to α_3'. However, such assignments must be made with caution, bearing in mind the 1–2-eV accuracy of the calculations and the rather arbitrary decomposition into four lines made by Parratt. We conclude that the accuracy of the nonrelativistic Hartree-Fock calculations of KS is generally supported by the RDF results, and, with a few minor exceptions, the present work also supports the transition assignments of that work.

TABLE VI. Transition assignments for the various features identified in the measured $K\alpha$ satellite of Cu.

Feature	Ref. [5]	Ref. [7]	This work	Ref. [4]
A	α'	h,b^*	h	g,h
B		g		
C		b	g	
D	α_3	a,a^*	b	b
E	α_4	f	a	a,f
F	α_3'	c	c,f	c
G		k	k	

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